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ACIDIC PRECIPITATION IN ONTARIO STUDY (APIOS)

AN OVERVIEW: THE CUMULATIVE WET/DRY DEPOSITION NETWORK

(2nd revised edition)

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Ontario
Ministry of the Environment

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Minister

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Deputy Minister

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PREFACE

Since the last publication of this document (April, 1984), the Acidic Precipitation in Ontario Study (APIOS) Cumulative Wet/Dry Deposition Network has undergone a number of changes to ensure that the deposition monitoring program continues to collect the highest quality data possible. This document has been updated to reflect these changes. For a detailed description of the APIOS Cumulative Wet/Dry Deposition Network's structure, operating and quality assurance procedures refer to the Technical and Operating Manual, (Bardswick, 1983) and the APIOS Quality Assurance Manual (Ontario Ministry of the Environment, 1985).

1. INTRODUCTION

The phenomenon of acidic precipitation has been recognized as a regional, provincial and international-scale perturbation of the environment. The Air Resources Branch (ARB) of the Ministry of the Environment (MOE) has established two monitoring networks which operate under the auspices of the Acidic Precipitation in Ontario Study (APIOS). The APIOS Cumulative Wet/Dry Deposition Network and the APIOS Event Wet/Dry Deposition Network have been designed to collect data so that a quantification of both wet and dry deposition patterns can be ascertained.

Although the primary concern for both networks is the measurement of deposition, they differ accordingly by the time resolution of their sampling periods. The event (used interchangeably with the term daily) network collects precipitation and air filter samples on a daily basis to investigate the characteristics and to determine the origin of pollutants deposited in these events, i.e. short-term wet and dry deposition patterns. The cumulative network monitors on a 28-day cycle (on a monthly basis from the network's inception in September, 1980 to January 5, 1982), collecting precipitation and air filter samples to measure long-term wet and dry deposition distributions.

Details of the event network are described elsewhere in "Acidic Precipitaton in Ontario Study (APIOS). An Overview: The Event Wet/Dry Deposition Network" (Chan et al., 1985). This document is available from the Air Resources Branch. No further discussion of this network will be given in this document.

The cumulative deposition network to be presented herein will be described according to its two components under the headings "Cumulative Wet Deposition Network" and "Cumulative Dry Deposition Network" respectively. The exceptions to this format are found in the sections entitled 'Network Design' and 'Network Siting Criteria and Sampling Locations', since a cumulative sampling site must fulfill the same requirements for both wet and dry deposition collection.

2. NETWORK OBJECTIVES

2.1 Cumulative Wet Deposition Network:

The objectives of this network are twofold:

1) To study the chemical composition of cumulative precipitation samples (collected on a 28-day cycle) within the Province.

2) To determine the long-term wet deposition distributions of various chemical parameters (both temporally and spatially) across the Province.

2.2 Cumulative Dry Deposition Network:

The objectives of this network are also two-fold:

1) To determine the ambient concentration of airborne acid-related pollutants on a cumulative (28-day) basis.

2) To infer dry deposition of these pollutants by using airborne concentrations (obtained by low-volume air filtration) with appropriate deposition velocity values in the relationship:

$$\text{Flux}(\text{ug m}^{-2}\text{s}^{-1}) = 100 \times C\ (\text{ug m}^{-3}) \times V_d\ (\text{cm s}^{-1})$$

where flux = dry deposition per unit area per unit time

C = 28 day mean concentration

V_d = average deposition velocity

Based on these estimates, the long-term dry deposition distributions of various chemical parameters (both temporally and spatially) across the Province can be derived.

3. NETWORK DESIGN

The design of the cumulative network is based on historical data from the Canadian Network for Sampling Precipitation (CANSAP) and on the results of MOE long-range transport computer modelling. The cumulative network was designed to satisfy the following objectives:

1) to provide long-term (seasonal/annual) data to determine deposition fields of acid, sulfur and nitrogen species and trace metals, based on cumulative (28-day) collections,
2) to provide for placement of samplers on spatial scales varying from local to regional to provincial,
3) to give special emphasis to sampling in areas of highest expected and known deposition and/or high susceptibility to acidic deposition.

The sampling program is conducted in five of the Ministry of the Environment's regions (regional offices in parentheses): the Southwestern region (London), encompassing the West-Central region; the Central region (Dorset); the Southeastern region (Kingston); the Northeastern region (Sudbury); and the Northwestern region (Thunder Bay). Because the steepest gradients in deposition exist in Southern Ontario, the density of samplers is highest there. The number of low-volume air samplers in each region is slightly less than those of the wet-only precipitation collectors because of smaller spatial variability in air quality data.

4. NETWORK SITING CRITERIA AND SAMPLING LOCATIONS

Based on the design criteria outlined in the previous section, all MOE regions were inspected for suitable sampling sites. Determining the actual locations involved fulfilling both the aforementioned spatial requirements as well as meeting site-specific requirements. The latter requisites are described briefly here.

The overriding consideration in site selection is the prevention of sample contamination. This is accomplished by locating sampling sites away from local sources of pollution so that the collected samples are regionally representative. In addition, the sampling instruments must be located at a site which has little or no potential for affecting the integrity of the collected samples, i.e. they must be clear of obstructions, and other site-specific sources of contamination nearby must be minimized. The following list summarizes the many sources of contamination that could affect the chemical integrity of samples, both wet and dry:

* urban areas (industrial activity, vehicular emissions, human activity)
* airports
* highways
* trees (obstructions, rain splash, organic debris, throughfall)
* buildings (obstructions, rain splash, emissions)
* unpaved roads (spray, salt, sand, airborne dust, vehicular emissions, snow ploughing, snow blowing)
* sewage treatment plants and aeration lagoons
* cultivated fields and orchards (herbicide and pesticide spraying, fertilizer emissions, airborne dust, organic debris)
* overhead wires
* oil or gas wells
* parking lots
* ground cover (rock, loose soil)
* marshes (emissions, insects)
* gravel pits
* salt or sand piles
* gardens

In addition to the minimizing of sample contamination, siting criteria must also incorporate factors which affect the logistics and operation of samplers. The major considerations are:

* site characteristics (ground cover should be grassy and flat, and as open and cleared as possible)
* avoidance of obstructions (adhere to a minimum "sampler-to-obstruction" distance of 2.5 times of the obstruction height)
* surrounding vegetation (windbreaks approximately 200 m away improve precipitation sampler collector efficiency)
* accessibility (easy access required but must be removed from roads)
* topography (locations near hills and depressions should be avoided)
* electrical supply must be available on-site
* safety (must be free from vandalism)
* personnel to regularly maintain sampler and collect samples.

To aid in a comprehensive evaluation of a site, a site criteria checklist (Appendix 1) is used. Acceptance of a site for sampling depends upon the meeting of most (if not all) of the siting criteria. To indicate the importance of proper siting in the APIOS program, site characteristics generally over-ride all other factors.

To date, thirty-seven sites have been chosen for automated precipitation collectors by applying the APIOS network siting criteria. In addition, one site in each region has a co-located collector as a measure of precision. Low-volume air samplers are located also at twenty-five of these sites. Again, one site in each region has a co-located sampler as a measure of precision. Some of the sites are located on Ministry of the Environment property while others are on private property. The actual sampling locations are shown in Figure 1 and listed in Table 1.

5. INSTRUMENTATION

5.1 Cumulative Wet Deposition Network:

Each cumulative deposition site is instrumented with an automated wet-only collector and a precipitation Nipher gauge (prior to the summer of 1984, a storage gauge was used as the precipitation depth gauge) to serve as a primary standard of the total precipitation occurred during a particular 28-day period (see Figure 2). The instrument used is a M.I.C. Type A wet-only precipitation collector (formerly manufactured by Sangamo). The standard manufacturer's instrument has been modified by Air Resources Branch to eliminate or reduce the effect of several problems. A description of the instrument and its major modifications follows.

The principal features of the M.I.C. Type A sampler are:

1) sensor grids (extending out from the body of the collector) for the detection of precipitation,

2) high-density polyethylene collection vessels, with a surface area of 324 cm^2, and

3) a moveable hood (when precipitation comes in contact with the sensor grids, the circuitry of the grids becomes closed, activating the instrument to expose the collection vessel for precipitation collection).

The major modifications to the M.I.C. Type A collector are as follows:

1) A pliable polyurethane foam gasket (a silicone rubber gasket was used prior to the summer of 1984) sealed in a polyethylene bag is attached to the stainless-steel underside of the moveable hood. Its purpose is to form a tight seal between the top of the collection vessel and the underside of the hood to minimize evaporative loss of the sample. In addition, the gasket stops contaminants from entering the sample through gaps between

the top of the vessel and the underside of the hood. The gasket is also very important for preventing metals contamination of the sample from the hood. Recirculation of sample water can occur as it evaporates inside the bucket, condenses on the underside of the hood, and ultimately drips back into the sample. With no gasket present, the condensate can leach metals from the steel surface and drip them into the bucket. Laboratory testing of this gasket indicates that there is negligible contribution of any chemical constituents of interest from the gasket to the sample.

2) The use of disposable polyethylene/nylon laminate-type bags (polyethylene bags were used before November, 1982) inserted into collector's buckets to serve as collection containers is a regular feature of the cumulative network. The use of bags as a collection medium is very desirable, primarily due to the reduction of potential contamination and sample handling associated with sample transfers and the elimination of cleaning of collection vessels. Desorption of chemical constituents from the bag surface has been found to be minimal. Although the bags present pristine environment for sampling precipitation, laboratory studies (Chan et al, 1983) and field observations have shown that long-term adsorption exists for the trace metals Fe, Al, Cu, Pb and Zn which can be recovered by mild nitric acid leaching.

3) A knife edge collar is attached to the top of the precipitation bucket after the bag is inserted. This clamps the bag in place and gives the sample container a very distinct, narrow edge. This, in turn, reduces rain drop splash and prevents the pick-up of particulates on the edge. The efficient seal between the hood gasket and knife edge serves to minimize evaporation.

4) The collection buckets are wrapped with aluminum foil to minimize evaporation.

5) To improve the efficiency of snow collection, namely by eliminating the blow-out of collected snow from the collection vessel under high wind conditions, a long bucket and bag for winter precipitation collection has been implemented. Wind tunnel testing at the University of Toronto (Haasz and Solomon, 1980) indicated that the use of a 1 m length collection vessel provides approximately a 4:1 height to diameter ratio, which would optimize the vessel's aerodynamic properties and is sufficient to minimize the snow blow-out effect. To accommodate this longer container, the bottom of the MIC Type A collector is cut out and an adjustable support base is attached to the standpost.

6) Standardization of the sensitivity and opening/closing response time of the precipitation collector has been made so that all samplers across the province respond similarly to a given precipitation type. Sensitivity is tested by special sensor grids outfitted with a 220 K ($\frac{1}{4}$W) ohm resistor. The timing control has been altered on the collector's integrated circuit so that the opening and closing of the hood is set at a two-minute delay ($\pm$30s).

Calculation of the total amount of wet deposition requires a knowledge of the sample chemistry and the total amount of precipitation that falls over the sampling period. Because the collection efficiency of the sampling instrumentation is less than perfect, the amount of precipitation collected in the sampler is not the true amount. Since most sampling sites do not have manpower on-site to operate standard precipitation gauges on a daily basis, each sampler is then accompanied by a Nipher-shielded precipitation gauge (similar in design to the Atmospheric Environment Service's Nipher snow gauge). This gauge accumulates precipitation over the sampling period and a depth measurement is taken when the sample is collected. In the 'wintertime' collection period (November to April) a 60%/40% mixture of methanol/ethylene glycol is placed in the gauge to melt the collected snow. To ensure the depth measurement is as accurate as possible, a capping layer of oil is placed in the gauge during the 'summertime' collection period (May to October) to prevent evaporation of the collected precipitation. The Nipher gauge's snow shield is removed during the 'summertime' to prevent splash.

5.2 Cumulative Dry Deposition Network:

In the beginning of the network operation, measurement of dry deposition was in the form of collection of dry fall samples in a dry bucket opposite the wet-only collection vessel of the MIC deposition collector. Similar to the wet deposition collection, polyethylene bags were used. In the summer of 1981, in an attempt to better assess the measurement of dry deposition on a cumulative basis, the APIOS program instituted the use of a low-volume air filtration system. As of June 1983, the dryfall measurement was discontinued entirely. This judgement was based upon the fact that samples collected in polyethylene bags were not representative of dry deposition, particularly for gaseous phase nitrogen and sulfur compounds. The high incidence of gross contamination was also a decisive factor in discontinuing the dryfall measurement. Hence only the low-volume air filtration technique is employed in the network to estimate dry deposition.

The long-term ambient air sampler used in the APIOS network is a Metrex Instrument Ltd AS-2 Low-Volume Air Sampler. The basic features of the instrument are i) a vacuum system controlled by a Gast heavy-duty diaphragm pump, in which the flow rate is controlled by a Dwyer Instruments VFA23 rotameter, ii) a temperature-compensated dry gas meter facilitates accurate monitoring of the flow and, iii) digital counters record associated total volumetric flow and operating time.

The vacuum system is used in conjunction with a modified 'Swinnex' two-stage, 47 mm polypropylene filter pack mounted at a 2 m height. The filter pack samples for 28 days (commencing at 0800h local time) at a flow rate of 2.0 litres per minute. Vacuum Jayon tubing connects the filter pack (mounted on a filter pack support plate and enclosed in a protective housing) to the vacuum system. The low-volume air filtration set-up is shown in Figure 3.

Within each filter pack there are three types of filters, each type specific for different chemical parameters of interest (Figure 4). The upstream filter is a 47 mm Whatman 40 cellulose filter, which is analysed for water-soluble sulfate, nitrate, ammonium, chloride, sodium,

magnesium, calcium, potassium, and the trace metals aluminum, manganese, iron, copper, nickel, lead, zinc, cadmium and vanadium. The Whatman 40 filter is followed by a Membrana (Ghia Division) Corporation 47 mm, 1 um Nylon filter, used for the selective adsorption of vapour phase nitric acid. Both filters are loaded in the upstream stage of the filter pack and are in direct contact with each other. The final filter type used is a pair of 50 mm Whatman 41 cellulose filters impregnated with a potassium carbonate/glycerol solution. This impregnating solution selectively absorbs sulfur dioxide (SO_2). These filters are loaded in the downstream stage and are also in direct contact with each other.

The filter pack sampling therefore provides integrated cumulative measurements of particulate-phase sulfate, nitrate, ammonium, a number of major ions and trace metals, as well as vapor-phase nitric acid and sulfur dioxide. There is some evidence that the speciation of the nitrogen compounds using this type of sampling scheme is subject to both positive and negative artifacts. It is felt, however, that the summation of the NO_3^- and HNO_3 on the W-40 and nylon filters respectively is an accurate measurement of total ambient nitrates.

6. SAMPLE COLLECTION AND HANDLING TECHNIQUES

6.1 Cumulative Wet Deposition Network:

Previously collection of cumulative deposition samples was made on the last-working-day-of-the-month. As of January 5, 1982 the APIOS program began collection of samples on Tuesdays (at 0800 hours local time) every 28 days. On the collection Tuesday, a structured sampling protocol is carried out by an on-site operator. This includes: i) removal of the collected sample, ii) cleaning of the instrument, iii) deployment of a new sample bag, iv) check of instrument performance, v) measurement of the Nipher gauge and vi) recording of observations. A brief synopsis of this protocol is given below.

On changeover dates, the site operator at each station activates the sensor and then stops the hood midway by switching the sampler off. The knife edge collar is then removed from the bucket. The sample is removed by grasping the portion of the bag above the bucket between the thumb and forefinger and lifting upward. As the bag is removed, it is squeezed at the point where the bag folds over the edge of the bucket. Excess air is purged out of the bag, then sealed with a twist tie.

Prior to the installation of a new bag, the instrument is thoroughly cleansed in an effort to minimize potential contamination. This requires the operator to wipe the sensor grids and, most importantly, the hood gasket and retaining collar with ethanol-soaked Kimwipes. A thorough rinsing with deionized-distilled water follows. The parts are then dried with Kimwipes.

To install a new bag, a new pair of sterilized polyethylene gloves are put on. The new sampling bag is fully expanded and then pushed into the bucket until it nears the bottom. The top of the bag is slid over the top of the bucket and then pulled down until it extends 3 inches down the outside of the bucket (i.e. that portion that has been handled). The retaining collar is then secured around the bag at the top of the bucket. At this point of the procedure, a new sterilized polyethylene glove must be put on. The operator must reach inside the bucket and flatten the bag against the inside and the top of the bucket. Extreme precaution is taken not to touch the collection surface with anything except the gloved hand.

After the bag has been changed, a brief check of the operation of the instrument is made. Once turned on, a check to see that the hood moves to cover the wet collection vessel (if the sensor grids are dry) is done. Other precautions taken include ensuring that a tight seal between the gasket and the collection vessel exists; activating the sensor grids to check that the hood moves to expose the collection vessel; checking the time taken for the hood to return (the response time should be approximately 2 minutes); and finally, ensuring that the sensor grids are warm to the touch.

The remaining task of the operator is to take an accurate precipitation depth measurement of the precipitation Nipher gauge. To calculate the amount of precipitation that fell during the collection period, the gauge must be measured at the beginning and end of the collection period, with the difference between measurements representing the fallen precipitation. In the wintertime collection period changes in the density of the methanol/ethylene glycol mixture in the Nipher gauge must be accounted for, thus it becomes necessary for the operator to record the mixture's temperature at the time of measurement.

As part of the APIOS Quality Assurance Program, all pertinent information regarding the sample itself is noted on an operator log-book and operator field sheet that accompanies each sample. If inconsistencies in sampler performance or serious problems affecting the sample's integrity exist, the APIOS technician responsible for the site is notified for corrective action.

Samples are picked up one week after collection from the on-site operators by APIOS technicians responsible for the samplers in their area (samples from the more remote sites in certain parts of the Province are shipped to the nearest regional MOE office). Samples are transported in coolers to a regional MOE office. Samples are visually inspected for organic debris, particulates and leaks, weighed for the determination of sample volume, properly sealed with a heat sealer, and then labelled. Samples are packed in coolers and shipped by courier service to the Laboratory Services Branch of the Ministry in Toronto, arriving the following day still cooled. In Toronto, samples are logged in and stored at $4^{o}C$ before chemical analysis.

6.2 Cumulative Dry Deposition Network:

The filter pack samples of this network are collected at the same time as the wet precipitation samples, i.e. on designated dates every 28 days at 0800 hours local time. The sampling protocol is as follows: prior to an upcoming sampling changeover day, an unexposed filter pack is loaded with Whatman 40, Nylon and K_2CO_3-glycerol impregnated Whatman 41 filters, sealed in a 'Whirl-Pak' polyethylene bag, then either shipped or taken to the sampling site. On changeover days, the low-volume sampler is shut-off and the associated sampling flow rate, flow volume and total time are recorded on operator field sheets. The exposed filter pack is covered with a new 'Whirl-Pak' bag, twisted off from the threaded nylon support plate and the bag sealed. The reverse of this procedure is carried out to mount the new unexposed filter pack. The digital counters on the low-volume sampler are reset to zero and the instrument is switched on to commence sampling.

Upon receipt at the regional MOE office, the filter packs are unloaded. The Whatman 40, Nylon, and Whatman 41 filters are folded into quarters and stored in separate 'Whirl-Pak' bags. All filters are labelled and then submitted to the Laboratory Services Branch in Toronto for chemical analyses.

7. CHEMICAL ANALYSES

7.1 Cumulative Wet Deposition Network:

All cumulative precipitation samples are analyzed for the following parameters: volume, conductivity, pH, total acidity, $SO_4^{=}$, $N\text{-}NO_3^{-}$, $N\text{-}NH_4^{+}$, Cl^{-}, Ca^{++}, Mg^{++}, Na^{+}, K^{+}, N-TKN (total Kjeldahl nitrogen), TP (total phosphorus), Zn, Fe, Ni, Cu, Pb, Al, Cd, Mn and V. The methods of analysis are given in Table 2.

7.2 Cumulative Dry Deposition Network:

The individual filters are analyzed for both water quality and inorganic trace constituents. The Whatman 40 filters undergo a deionized-distilled water extraction. The extract is split into two equal aliquots, with one portion analyzed (after an oven digestion in HNO_3) for Al, Mn, Fe, Cu, Ni, Pb, Zn, Cd, V, Ca^{++} and Mg^{++}. The remaining aliquot is analysed for $SO_4^{=}$, $N\text{-}NO_3^{-}$, $N\text{-}NH_4^{+}$, Cl^{-}, Na^{+} and K^{+}. From the nylon filter, $N\text{-}HNO_3$ (as nitrate) and $SO_4^{=}$ is determined; and SO_2 (as $SO_4^{=}$) is determined from the impregnated Whatman 41 filters. The observed $SO_4^{=}$ on the Nylon filters is added to that on the Whatman 41 filters to determine SO_2 concentrations. Methods of extraction and analysis are given in Table 3.

8. DATA HANDLING AND ANALYSIS

8.1 Cumulative Wet Deposition Network:

The reporting of chemical analysis is structured such that laboratory-approved data are entered from the Laboratory Information System (LIS) into the Ministry's Sample Information System (SIS) data base. A particular submission's supporting field data are merged with the corresponding chemical data. Before the results are finalized, the data are screened for ionic balance testing, exceedance of range tests, theoretical vs. observed pH and conductance, and Dixon-ratio statistical testing (comparison of chemical values for designated geographical regions over the same time interval). Validation flags may be appended to individual analytical results to indicate failure of these tests.

Analysis of the data involves the calculation of cumulative wet deposition rates as the product of pollutant concentration times the true precipitation depth. Reports of cumulative concentration and deposition data listings, annual statistics and interpretations are published on a regular basis.

8.2 Cumulative Dry Deposition Network:

Data for dry deposition are entered into the database in the same manner as that of wet data. Anomalous data are flagged by various office comments.

These data are screened primarily by exceedance of range and Dixon-ratio tests. Reports similar to those of wet samples are published on a regular basis.

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FIGURE 1

LOCATION OF APIOS CUMULATIVE WET/DRY DEPOSITION NETWORK SITES

1. Colebeater*
2. Merlin
3. Pt. Stanley*
4. Wilkesport*
5. Alvinston
6. Huron Park
7. Waterloo
8. Palmerston*
9. Shallow Lake*
10. Milton (removed March 1984)
11. Uxbridge*
12. Coldwater
13. Campbellford*
14. Cloyne*
(replacing Kalador, June 1983)
15. Smith's Falls*
16. Dalhousie Mills*
17. Golden Lake*
18. Wilberforce
19. Whitney
20. Dorset*
21. McKellar*
22. Mattawa*
23. Killarney*
24. Bear Island
25. Gougands*
26. Azure Lake
(replacing Ramsey, June 1983)
27. Moonbeam*
28. Attawapiskat
(removed February 1984)
29. Winisk
30. Geraldton*
(replacing Nakina, August 1983)
31. Dorion*
32. Quetico Centre*
33. Lac la Croix
34. Experimental Lakes Area
35. Ear Falls*
36. Pickle Lake*
37. Turkey Lake*
38. Moosonee*
(installed October, 1985)
39. Otter Island*
(operated only during "summer" periods)

* indicates both a dry and wet deposition network site

FIGURE 2:

INSTRUMENTATION USED IN APIOS CUMULATIVE WET DEPOSITION MONITORING

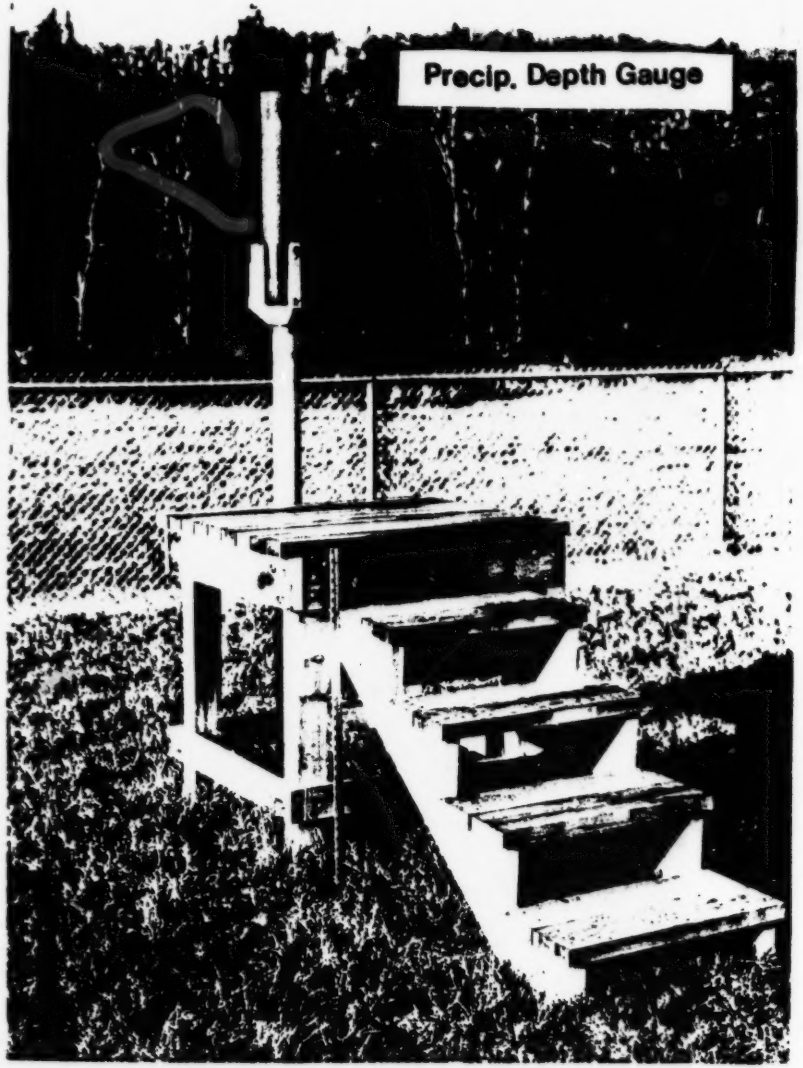

FIGURE 3:

INSTRUMENTATION USED IN APIOS CUMULATIVE DRY DEPOSITION

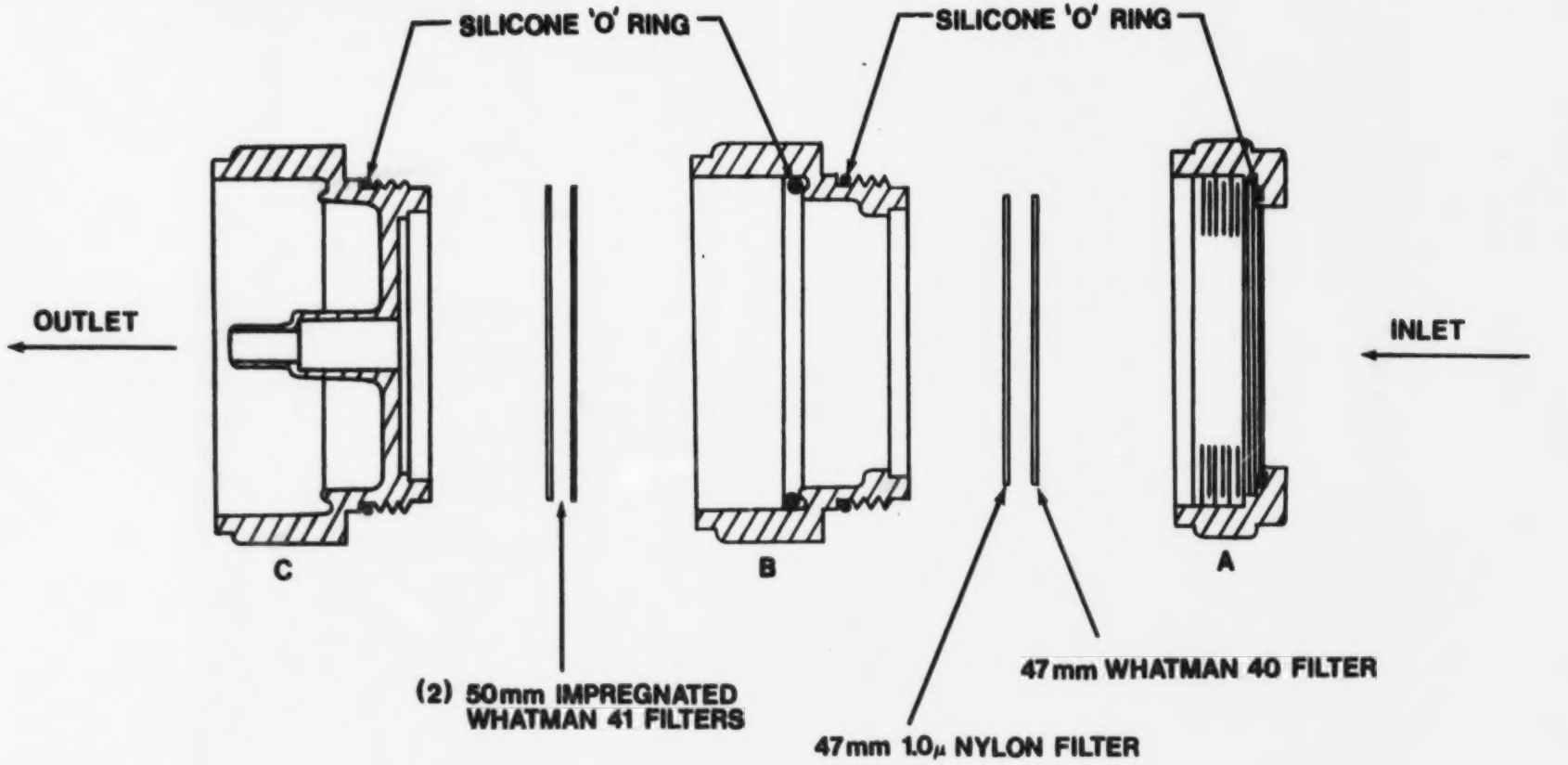

FIGURE 4:

CONFIGURATION OF FILTER TYPES USED IN APIOS CUMULATIVE DRY DEPOSTION MONITORING

TABLE 1

APIOS CUMULATIVE WET/DRY DEPOSITION NETWORK SITE DESCRIPTIONS

MOE REGION	STATION NAME	STATION NUMBER	INSTRUMENTATION	ELEVATION (m above MSL)	LATITUDE (North)	LONGITUDE (West)	UTM GRID CO-ORDINATES (Northing)	(Easting)
Southwestern	Colchester	1041	MIC/Low-Volume Air	183	41°59'15"	82°55'41"	4650000	340300
	Merlin	1051	MIC	191	42°14'47"	82°13'30"	4676400	398950
	Pt. Stanley	1061	MIC/Low-Volume Air	213	42°40'22"	81°09'55"	4724050	486700
	Wilkesport	1071	MIC/Low-Volume Air	183	42°42'11"	82°21'13"	4728350	389150
	Alvinston	1081	MIC	221	42°49'36"	81°50'04"	4942000	431550
	Shallow Lake	1091	MIC/Low-Volume Air	229	44°34'54"	81°05'24"	4936200	492850
	Palmerston	1101	MIC/Low-Volume Air	389	43°48'19"	80°54'12"	4850050	507750
	Huron Park	1191	MIC	250	43°17'28"	81°30'03"	4793000	459350
	Waterloo	2021	MIC	343	43°28'39"	80°35'09"	4813750	533500
Central	Dorset	3011	MIC/Low-Volume Air	320	45°13'26"	78°55'52"	5009650	662400
	Milton	3051	MIC	221	43°31'05"	79°55'54"	4818600	586350
	Uxbridge	3061	MIC/Low-Volume Air	244	44°12'46"	79°12'38"	4896800	643000
	Wilberforce	3071	MIC	396	45°00'54"	78°12'58"	4988150	719400
	Campbellford	3081	MIC/Low-Volume Air	175	44°17'28"	77°47'33"	4907600	277150
	Coldwater	3101	MIC	280	44°37'31"	79°32'08"	4942200	615900
Southeastern	Kaladar	4051	MIC/Low-Volume Air	244	44°41'31"	77°09'18"	4950800	329250
	Smith's Falls	4061	MIC/Low-Volume Air	122	44°56'41"	75°57'48"	4977100	423950
	Dalhousie Mills	4071	MIC/Low-Volume Air	69	45°19'00"	74°28'13"	5018100	541550
	Golden Lake	4081	MIC/Low-Volume Air	160	45°36'48"	77°13'03"	5053200	328400
	Cloyne	4091	MIC/Low-Volume Air	259	44°49'09"	77°11'45"	4964750	327100
Northeastern	McKellar	5011	MIC/Low-Volume Air	244	45°30'57"	79°55'19"	5040600	583950
	Killarney	5021	MIC/Low-Volume Air	183	45°59'26"	81°29'18"	5092900	462200
	Mattawa	5031	MIC/Low-Volume Air	198	46°16'45"	78°49'19"	5127150	667800
	Bear Island	5041	MIC	305	46°58'22"	80°04'40"	5202400	570350
	Ramsey	5051	MIC	427	47°26"33"	82°20'14"	5254900	399200
	Gowganda	5061	MIC/Low-Volume Air	343	47°39'04"	80°46'32"	5277300	516600
	Moonbeam	5071	MIC/Low-Volume Air	244	49°19'16"	82°08'46"	5463600	416650
	Attawapiskat	5081	MIC/Low-Volume Air	9	52°56'00"	82°24'00"	NA	NA
	Whitney	5091	MIC	412	45°32'21"	78°15'35"	5045950	713950
	Turkey Lake	5141	MIC/Low-Volume Air	472	47°03'15"	84°24'00"	5214250	696750
	Azure Lake	5151	MIC	244	47°28'12"	81°52'30"	5257650	434250
	Moosonee	5161	MIC/Low-Volume Air	8	51°12'34"	80°42'20"	5673000	520550
Northwestern	Dorion	6011	MIC/Low-Volume Air	244	48°50'33"	88°36'45"	5410800	382150
	Nakina	6021	MIC/Low-Volume Air	320	50°10'38"	86°42'90"	5556150	520950
	Ear Falls	6031	MIC/Low-Volume Air	350	50°38'31"	93°13'13"	5609800	484150
	Pickle Lake	6041	MIC/Low-Volume Air	360	51°27'41"	90°12'04"	5704800	694550
	Lac la Croix	6061	MIC	368	48°21'14"	92°12'32"	5355900	558400
	Quetico Centre	6071	MIC/Low-Volume Air	420	48°44'24"	91°12'08"	5399750	632100
	E.L.A.	6091	MIC	123	49°39'22"	93°43'28"	5500950	447350
	Winisk	6101	MIC	9	55°12'00"	85°08'00"	NA	NA
	Otter Island	6111	MIC/Low-Volume Air	204	48°06'50"	86°04'25"	5328750	569500
	Geraldton	6121	MIC/Low-Volume Air	351	49°48'05"	86°46'00"	5516300	516750

TABLE 2

APIOS CUMULATIVE WET SAMPLE LABORATORY ANALYSES

PARAMETER	ANALYSIS METHOD	DETECTION LIMIT (mg l^{-1})
pH (for H_f* determination)	Radiometer pH meter and Ingold low-conductivity combination pH electrode	0.01 pH units
Total Acidity (for H_t+ determination)	Gran titration: NaOH titration to a series of inflection points; results presented as ug l^{-1} as H^+	0.01
Conductivity	Radiometer conductivity cell and meter	0.1 us/cm
$SO_4^=$	Ion Chromatography	0.05
$N\text{-}NO_3^-$	Ion Chromatography	0.01
Cl^-	Ion Chromatography	0.01
$N\text{-}NH_4^+$	Automated phenate-hypochlorite colorimetry	0.005
Ca^{++}	Flame Atomic Absorption	0.01
Na^+	Flame Atomic Absorption	0.005
K^+	Flame Atomic Absorption	0.005
Mg^{++}	Flame Atomic Absorption	0.005
N-TKN	Automated phenate-hypochlorite colorimetry	0.06
TP	Ammonium molybdate-ascorbic acid colorimetry	0.006
Zn	Inductively Coupled Plasma	0.001
Fe	Inductively Coupled Plasma	0.001
Ni	Flameless Atomic Absorption	0.0002
Cu	Inductively Coupled Plasma	0.0002
Pb	Flameless Atomic Absorption	0.001
Al	Inductively Coupled Plasma	0.005
Cd	Flameless Atomic Absorption	0.00002
Mn	Inductively Coupled Plasma	0.001
V	Inductively Coupled Plasma	0.0004

* H_f - Free hydrogen ion concentration
+ H_t - Total hydrogen ion concentration

TABLE 3

APIOS CUMULATIVE LOW-VOLUME AIR FILTER LABORATORY ANALYSES

PARAMETER	FILTER TYPE	EXTRACTION METHOD	ANALYSIS METHOD	DETECTION LIMIT (ug filter^{-1})
Zn	Whatman 40	20 minute ultrasonic bath in 50 ml deionised/distilled water followed by oven digestion in 5% HNO_3	Atomic Absorption Graphite Furnace	0.050
Fe	Whatman 40	Same as above	Atomic Absorption Graphic Furnace	0.050
Ni	Whatman 40	Same as above	Atomic Absorption Graphic Furnace	0.010
Cu	Whatman 40	Same as above	Atomic Absorption Graphic Furnace	0.010
Pb	Whatman 40	Same as above	Atomic Absorption Graphic Furnace	0.050
Al	Whatman 40	Same as above	Atomic Absorption Graphic Furnace	0.250
Cd	Whatman 40	Same as above	Atomic Absorption Graphic Furnace	0.001
Mn	Whatman 40	Same as above	Atomic Absorption Graphic Furnace	0.050
V	Whatman 40	Same as above	Atomic Absorption Graphic Furnace	0.020
$SO_4^=$	Whatman 40	Same as above	Ion Chromatography	2.00
$N\text{-}NO_3$	Whatman 40	Same as above	Ion Chromatography	0.50
$N\text{-}NH_4$	Whatman 40	Same as above	Automated phenate-hypochlorite colorimetry	0.250

TABLE 3 (Cont'd)

APIOS CUMULATIVE LOW-VOLUME AIR FILTER LABORATORY ANALYSES

PARAMETER	FILTER TYPE	EXTRACTION METHOD	ANALYSIS METHOD	DETECTION LIMIT (ug filter^{-1})
Cl^-	Whatman 40	20 minute ultrasonic bath in 50 ml deionised/distilled water followed by a oven digestion in 5% HNO_3.	Ion Chromatography	0.50
Ca^{++}	Whatman 40	Same as above	Inductively Coupled Plasma	1.0
Mg^{++}	Whatman 40	Same as above	Inductively Coupled Plasma	0.025
Na^+	Whatman 40	Same as above	Atomic Absorption Spectrophotometry	0.250
K^+	Whatman 40	Same as above	Atomic Absorption Spectrophotometry	0.250
N-HNO_3	Nylon	20 minute ultrasonic bath in 25 ml 3 x 10^{-3} N NaOH	Ion Chromatography (as NO_3^-)	0.25
SO_2	Nylon	Same as above	Ion Chromatography (as SO_4^-)	1.0
SO_2	Whatman 41	60 minute shaking in 50 ml 0.05% (v/v) hydrogen peroxide; followed by 20 minute ultrasonic treatment; followed by making up to 50 ml with hydrogen peroxide	Ion Chromatography (as SO_4^-)	1.65

APIOS SITE DESCRIPTION QUESTIONNAIRE

Date: _____

COMPLETED BY: _____

REVISION NO: _____

Type of Site
(check one)

__ Existing Site (regular network)

__ Potential Site

__ Special Study Site

1. SITE IDENTIFICATION

Cumulative Wet _____ Cumulative Dry _____

Event Wet _____ Event Dry _____

Other (describe) _____

Station Name _____ Station Number _____

MOE Region _____ County _____ Township _____

Latitude ____ o ____ ' ____ " Longitude ____ o ____ ' ____ " Elevation ____ m

UTM Co-ordinates E N

Name of Primary Operator _____

Alternate Operator _____

Regional Technician _____

Mailing Address (Primary Operator)

_____

_____

_____

Phone (Primary Operator) ____/____ (Res) ____/____ (Bus)

Phone (Alternate Operator) ____/____ (Res) ____/____ (Bus)

Nearest APIOS Site Cumulative: Station Name _____

Distance _____ km

Event: Station Name _____

Distance _____ km

2. **LIST OF INSTRUMENTATION** (if applicable)

1) Instrument Type: _____

Cumulative Wet: _____ Cumulative Dry: _____

Event Wet: _____ Event Dry: _____

Other (describe): _____

Manufacturer: _____ Model #: _____

2) Instrument Type: _____

Cumulative Wet: _____ Cumulative Dry: _____

Event Wet: _____ Event Dry: _____

Other (describe): _____

Manufacturer: _____ Model #: _____

3) Instrument Type: _____

Cumulative Wet: _____ Cumulative Dry: _____

Event Wet: _____ Event Dry: _____

Other (describe): _____

Manufacturer: _____ Model #: _____

1) Standard Gauge Type _____

2) Standard Gauge Type _____

Other _____

_____

_____

_____

cont'd

3. SITE LOGISTICS

1) Is road access to site in summer: _____ good _____ fair _____ poor?

winter: _____ good _____ fair _____ poor?

2) Type of road surface? (dirt, gravel, oiled, paved) _____

3) How far is the primary collector from road access? _____ m

4) If necessary, how close can a vehicle approach the collector? _____

5) If no road access to site, how is site reached? (plane, snowmobile) _____

6) What is the available electrical power at site? _____

Volts _____ Amps _____ No. of circuits _____

7) Is the circuit on a: Receptacle GFIC _____ _____

Circuit Breaker GFIC _____

No GFIC _____

Battery _____

8) What is the distance from collector receptacle (or proposed site) to circuit panel?

_____m

9) What are the number of power failures per month? _____

per year? _____

10) Are there any other logistical problems which prevent the sampling site being easily approached or operated?

(locked gate, guard dog, flooding in spring?)

_____

_____

_____

4. TOPOGRAPHY AND LAND USE

1) Ground slope at site: _____ %

2) Ground cover within 15 m of sampler (grass, scrub, gravel, sand, soil)

_____

3) Soil type within 10 m of site (sand, topsoil, clay, rocky)

_____

Soil type within 500 m of site (sand, topsoil, clay, rocky)

_____

4) Land use % near site, within 1 km/10 km

% Cultivated _____/_____

% Orchard _____/_____

% Lawn _____/_____

% Pasture _____/_____

% Forest _____/_____

% Water _____/_____

% Other (describe) _____/_____

Type of Cultivated crop(s) _____

Forest types within 1 km of site _____

5) What types of windbreaks are within 200 m of primary sampler (buildings, trees, hills) _____

6) Indicate any windbreaks within 200 m of primary sampler (Mark what quadrants of the compass have a windbreak)

7) Prevailing wind direction during event (according to Operator)

Winter _____ o

Summer _____ o

8) Comment on local topography (i.e. flat, hilly, river, basin, etc.)

_____

_____

_____

_____

_____

_____

9) Cultivated Land Use

Type of Crop	Type of Herbicide or Insecticide Used and when applied	Type of Fertilizers and when applied	Future Crops	Distance to Crops	Direction to Crops

cont'd

10) Any planned land use in future? _____

_____

_____

11) In winter is there any evidence of drifting snow? _____

12) Tall objects near sampler:

i) Trees _____ (species) Max Height _____ m

Distance _____ m Direction _____ o

ii) Buildings _____ (type) Height _____ m

Use _____ Type of Heating _____ Distance _____ m

Direction _____ o

iii) Other (overhead wires, telephone poles, hedges)

A) Object _____ Height _____ m

Direction _____ o Distance _____ m

B) Object _____ Height _____ m

Direction _____ o Distance _____ m

C) Object _____ Height _____ m

Direction _____ o Distance _____ m

D) Object _____ Height _____ m

Direction _____ o Distance _____ m

Comments _____

_____

_____

_____

_____

_____

_____

5. HUMAN ACTIVITY

1) Large highways (expressways): Distance _____ (Km, m)

Route # _____ Direction from Sampler _____

2) Other paved roads: Distance _____ (Km, m)

Direction from sampler _____

traffic: Heavy _____, Medium _____, Light _____

3) Unpaved road: Distance _____ (Km, m)

Direction from sampler _____

traffic: Heavy _____, Medium _____, Light _____

Surface (dirt, gravel, oiled) _____

4) Parking lot: Distance _____ (Km, m)

Direction from sampler _____

Unpaved _____ Surface material _____ Use: Continuous _____

5) Lake/river or rail traffic: Distance _____ (Km, m)

Direction from sampler _____ barge _____

lake steamer _____ rail _____

traffic: Heavy _____, Medium _____, Light _____

6) Snow clearing procedures:

Type of surface (road, parking log, hwy, walkway)	Surface distance from sampler	Direction from sampler	Snow Control (plowed, sanded, blown, salted-with what?)

7) Airport(s): Distance _____ (Km, m)

Direction from sampler _____ Name _____

traffic: Heavy _____, Medium _____, Light _____

traffic type: _____

8) Stationary sources:

Power plant(s): Distance _____ (Km, m)

Direction from sampler _____ Fuel (gas, coal) _____

Electrical Capacity _____ (KW_e, MW_e)

Light industry: Name _____ Distance _____ (km)

Direction from sampler _____ Product _____

Heavy industry: Name _____ Distance _____ (km)

Direction from sampler _____ Product _____

9) Other sources: Significant agricultural operations:

Distance _____ (Km, m)

Direction from sampler _____

Other (please describe) _____

_____

Distance _____ (Km, m)

Direction from sampler _____

Other could include - gravel pits, sewage lagoons, marshes, MTC,

Salt or Sand piles - (see Topographical Maps)

cont'd

10) Effects from local cities, towns, or villages (population)

A	100,000
B	10,000
C	5,000
D	1,000

NAME	POPULATION (letter code)	DISTANCE	DIRECTION	TYPES OF POLLUTION SOURCES

6. SITE SUMMARY

List deviations from site criteria and all advantages and disadvantages of this site.

(use reverse side if necessary)

7. SITE LOCATION

1) A topographic map (Scale 1:50,000) indicating sample site with a Red X.

- arrows on top map indicating best approach from nearest "MAIN" Highway.
- indicate with red dots any major sources of pollution of contamination (industry, gravel pits, towns)

2) A concise description on how to reach this site. (below)

8. SITE DIAGRAM

1) Notable Items (mark all distances)

1. North
2. Direction of prevailing winds
3. Windbreaks
4. Roads (with names)
5. Parking lots
6. Buildings (indicate type of heating)
7. Potential contamination sources
8. Ground cover (grass, scrub, soil, sand)
9. Trees/hedges/marshes
10. Obstructions (include height): poles, towers
11. Topography
12. Water
13. Crops/gardens
14. Paths (foot, snowmobile, ski)
15. Location of existing hydro facilities
16. Position of sampler(s)
17. Nature of soil (rocky, sandy, clay)

2) Legend

Coniferous trees (include height, H=)

Deciduous trees (include height, H=)

Wooden fencing (include height, H=)

Wire fencing (include height, H=)

Grass

Direction of ground slope

Bushes/hedges (include height, H=)

Buildings (height and heating)

Railway tracks

9. **SITE PICTURES** (Indicates site name, compass point and date of photograph on back of all slides)

1) Two pictures are to be taken so as to best include all sampling instrumentation on site. If possible take pictures 90° apart from each other. Indicate on Site Diagram as P1 and P2 where the pictures were taken from. Also, identify each picture on a list of photographs.

2) Take four pictures showing the area surrounding the site. These should be taken at four compass points from just behind primary sampler facing in the direction of the compass point.

3) Special pictures showing nearby potential sources of contamination (e.g. salt pile) that may affect the site are to be taken. These should be indicated, if possible, on a site diagram as SP1, SP2, etc. with a description of the picture on the back of the print.

LIST OF PHOTOGRAPHS

#	Direction Facing	Comments

6AR14-Fig.25